#### 母公開特許公報(A) 昭63-271938

@int\_Cl.\* H 01 L B 08 B G 03 F 21/304 7/00 1/00

滋別記号 **广内整理委号**  ④公開 昭和63年(1988)11月9日

D-7376-5F 6420-3B Z-7204-2H 響査請求 未請求 発明の数 1 (全 4 頁)

硬衰面の洗浄方法 砂発明の名称

②特 四 昭62-106069

受出 頭 昭62(1987)4月28日 進 苺 昭 則

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1. 発明の名称

優製面の気が方法

2. 特許請求の範囲

存成系異物が存在する壁表面を挟作数により表 かした後に乾燥する洗浄方法において、前記洗浄 誰による状界の任意の工程の前に救犯硬表面に無 外担を囚引する工程を設けたことを特徴とする領 裏面の後海方は、

1. 発明の詳細な説明

〔農衆上の利用分野〕

本丸明は硬直面の洗浄方法に係り、詳しくは、 例えば半導仏プロセスにおいてフォトマスクブラ ンクやフェトマスク、あるいは半導体基板等を抗 カするむ台に用いられる歴式秩序方法に関する。 (世界の故事)

姓来この種の遊式牧浄方法としては、一般に、 被抗療物を少なくとも2種以上の秩序線(例えば 硫酸、純水、アルコール等)に吸次投資し、必要

に応じて抗浄液中に超音波を伝鞭させて抗浄処理

した後、アルコール等の意気により気が衰そ気化 し松乗する方法が知られている。

【発明が保険しようとする問題点】

しかしながら、上記した歴式表疹方法により被 旅り 知を決かい返した 観合、 洗り 処定 したに もあ らず、状が処理機の施佐が物に行れの存在が益め られる。その「原因として、誰状や物上に囚むして いる我哲レグスト智の有能系異物が上記法が幻想 によって完全には散去されずに洗炉処理後し被洗 作物上に一部残留することが挙げられる。また他 の気因として、被抗を物上に囚者している税包レ ツスト等の存職系異物が氏序処理に用いられる数 設置等の技序器と化学反応して独族序物の表面に 新たな反応生成者として比着することが挙げられ る。さらにもう1つの原因として、あか処理にお いて用いられる異なる種類の洗浄波の化学反応に より、被洗押物の表面に新たな反応生成物が生じ ることが挙げられる。この異なる種類の先子披拜 心の化学反応による行れの死生について更になり 的に述べると、この種の独洗が他の洗浄処理には、

上述の如く従来の数式洗浄方法では、被洗浄物の表面に固想している有機系典物からなる時代を完全に飲ますることは固貫であり、この有機系典物と洗浄地との反応、洗浄地図志の反応により新たな所れが被洗浄物の表面に発生するという問題をがあった。

物が残留することがない。

また常外級限例処理によって前記の有機系異物は状序線による秩序処理時に被抗浄物の表面上に 点印存在していないので、有機系異物と秩序数と の化学反応により折たな反応生成物が被秩序物表 版上に形成状限することもない。

【食品册】

本党司は、こ ような問題点を解決するためになされたものであり、その目的は、被洗浄物の表質に囚打した打理系質物からなる所れを完全に改生し取ると共に洗浄地理に作う折たな時れの発生のない水浄方法を最低することにある。

[四周点を解決するための手段]

本見明は、上記目的を達成させるためになされたものであり、有機系具物が存在する硬長面を洗浄をより洗浄した後に乾燥する洗浄方法において、前記洗浄法による洗浄の任意の工程の音に前記を表面に無外数を取引する工程を設けたことを特徴とするものである。.

(#M)

統庁譲による秩序前に被抗浄物に食外数を削引することにより、被秩序物の表面に残倒しているフェトレジスト等の有限系質物が化学変化を受け、その名で分解質失したり、その名の秩序変による 洗浄処理において秩序数によって溶解又は剥削し やすい状態になるので、被洗浄物の技序数による 洗浄処理機に被秩序物の表面上に前記の有数系数

被状序物の収度秩序、純水状序及びイソプロピルアルコール(以下『PAと昭称する)状序を順次行なった額、被洗浄物を『PA証例を用いて化型する従来のフォトマスク状形方法において、被避決市前に被洗浄物を繋外線照射処理する文語例について以下に製削する。

被比が物として、周知のレジストエ記、エッチングエ母およびフォトレジスト制能工程を登抜けられたフォトマスクを用いた。すなわち、被抗作物であるフォトマスクは、選光性ガラス基を上にクロム基光性機を被引してなるフォトマスフィンクとにポジタフォトレジストであるはバターンを引起した後、マンクとして対比、変更した後、マンクルにボターンをマスクとして選先を設定をよったのである。

このフォトマスク(大きさ5×5×0,09インチ)4枚を、低圧水銀灯を異視してなる意外和 型別装置(処理室容額:3240m<sup>3</sup>)内に配置 し、素外数原製処理を行なった。

弘元条件は、以下の造りである。

男外の似… 2537人の原稿の包皮が全体の 90%、1849人の舞蹈の強度が ◆はの最%である低圧水型気を用い

低圧水型灯に供給する数パワーー770W . ウェットエアー…常外ぬ似的装置のガス導入口 から301/分の装造で導入した。 ウェットエアーは紫外線機関数に 0、の発生効率を向上させる作用を

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気外袋煎引動を後の並洗を物を次いで洗浄型屋 し、松煌知思した。すなわち、抗彦処理は、被抗 かもを確立98%の歴集後1権に5分間長頭し、 次に美水1倍に30秒間提及し、更に「PA1倍 に3分回提思することにより行なった。なお値 **抗市物のIPA種接頭に際しては、IPA腋中に** 出る故(45kiiz と46kiiz の周被散を交互に義 り乗し乳生する乳質器を使用した。パワーは40 OWである。) を伝戴して超音放光がを行なった。 兼配 洗浄処理協の統領処理は1PA的から引 を上げられた雑族が物を1PA意気に延介するこ とにより行なった。

上記の仰く葉外間照射処理機に洗浄、乾燥処理 された雑洗浄物16枚について、その状态化の位 合を担償したが、18枚ともに方れが思められな かった.

なお、素外線型引動配を行なわずに同様の状態。 松桑処理を行なった被洗浄物15枚についても剪 はにその爪巾をの収合を設立したが、15枚とも に全面に汚れが思められた。また皮が処理におい て美水便能抜炸処理を3時とし、各根投資時間を それぞれ100岁としても、無外数を虹別しない 着合には放洗浄物の全面に汚れが深められること

この支持側の結束から、無外数規制処理を行む う本発明の方法によれば、被洗浄物表面上に固む している有理系集物が効果的に放去されており、

かつ状存植環時の化学反応に伴う新たな反応生成 もの発生もないので、抗抑処理機の破滅抑制の環 かせが十分に数なされることが明らかである。

上の変換的では独族が物として、ボジ型(光分 解型)フォトレジストが抵留囚着しているフォト マスクを用いたが、本発明の方法においてはネガ 型(光変化型)フォトレジストが残骸回着してい る旅技が物を洗浄処理するこもでき、またレジス トがポツ型及びネガ型電子器レジストであっても

また本苑明の方近は、フォトマスクの表声に截 足されるものではなく、フォトマスクプランク、 ・ガラスは収、送引導電影付きガラス基板、シリコ ンウェハ等、更にほカメラレンズ等の光学レンズ や股袋レンスを被抗浄物とし、これらの食器に付 巻乃至囚若している有機系異物(例えば大気中の こみに山来する汚染物や手根接触による月染物等) を重好することが望せしい。 を除去するためにも用いられる。

また紫外線図引条件は、雑鉄炉物の材質及び鉄 市場理前に経てきた工程等により譲食選定しうる。 意外格限制処理時期はこれに担定されるものでは

すなわら、常外間を照明する先輩として、水田ア ~クランプ、中圧水量ランプ、高圧水塩ランプ、 キセノンランプ、低ホランプ界を用いてもよく、 また導入ガスとして、上の支援側で用いたウェッ トエアーの代りにドライエアーやオソン(0,) 等を使用しても良く、さらにパワー、処理時間を も任意に変勢させることができる。また起来なの ガスを含有する雰囲気中で業外値を放射しても良 く、この名合には開業が無外線型効気にオゾンに なって、被抗が物上に付着している汚れ成分の簡 化分解等が促進される。またアルゴン、拡展すの 不抵性ガスを含有する雰囲気中で無外線を取引し ても良い。心部する意外心の故及は上の文語例に 記したもの以外に任意の独臣であってよいが、有 概象での異物を効果的に減少・原去せしめるため には1000~3000人の放展を有する無外路

また上の支施房では、緩破疾症に先立って黒外 雑型別処理を行なったが、木見巾の方法において、 なく、製配抗力性で純水抗作的または純水及力性で 1 PA 洗浄的に無外線照射処理を実施しても食く、また例えば発療洗浄的及び破離抗浄機で純水洗浄的の組く集外機照射処理を 2 個以上行なっても良い。

もちろん雑洗を物の洗浄波中への浸漉洗浄に際

スク、フォトマスクプランク、ガラス基板、手導体基板等、更には光学レンズや難関レンズ等の硬 表面を有する製品を効果的に指ひ化することを実 関するものであり、その工業的重視は極めて多大 である。

特許出職人 本一 7 些 式 会 社代理人 弁理士 中 将 都 男

して、美界投中に超点法を伝掘させたり、あるい は世間の毎年延備させたりすることは任意である。

また乳の物理として、上述の雑誌の物を乳の数 中に設置する方法の代りにスピンナー等で被求が 物を回転させながら洗予数をスプレーする方法や 雑洗予物に加圧(百圧ジェット化)された洗浄線 を助きつける方法などを拡加することもできる。

上の実施例では被決が物の乾燥を埋として、 I P A 磁気による超気を増を採用したが、 フロンギ の他の温気を用いる温気を増でも良く、またスピ ン乾燥でも良い。

本見切の方はは、意外範型的処理を行なわない 通常の状形方はを支援した結果、異なる砂質の表 多様(何えば硫酸とアルコール)の化学反応によ る時れが発生した複批が物の可洗浄のためにも有 熱であり、展外節型耐処理機に洗浄酸による可決 浄処理を行なうことによって、適常の条件では飲 去個質な汚れを除去することが可能である。

〔段明の効果〕

以上非難したように、木丘明の方法はフェトマ

Japanese Patent Laid-Open No. 63-271938

Laid-Op n Date: November 9, 1988

Application No. 62-106069

Application Date: April 28, 1987

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### SPECIFICATION

1. Title of the Invention: METHOD FOR CLEANING HARD SURFACE

# 2. Claim

A method for cleaning a hard surface having organic foreign substances, comprising cleaning the hard surface with a cleaning solution, followed by drying, wherein a step of irradiating the hard surface with ultraviolet light is provided before any given step of cleaning with the cleaning solution.

Detailed Description of the Invention [Industrial Field of the Invention]

The present invention relates to a method for cleaning a hard surface, and more particularly relates to a wet cleaning method which is used, for example, when a photomask blank, a photomask, a semiconductor substrate, or the like

is cl aned in a semiconductor process.

[Description of the Related Art]

The known wet cleaning method generally includes the steps of cleaning by immersing a workpiece to be cleaned in at least two cleaning solutions (e.g., sulfuric acid, pure water, and alcohol) one after another, and as required, by propagating ultrasonic waves into the cleaning solutions, and then drying by vaporizing the cleaning solutions by means of vapors of alcohol or the like.

[Problems to be Solved by the Invention].

However, when a workpiece is subjected to cleaning treatment by the wet cleaning method described above, the workpiece after cleaning is observed to have contamination in spite of the cleaning treatment. One of the reasons for this is that organic foreign substances such as a residual resist stuck on the workpiece are not completely removed by the cleaning treatment and partially remain on the workpiece after the cleaning treatment. Another reason is that organic foreign substances such as a residual resist stuck on the workpiece chemically react with a cleaning solution such as concentrated sulfuric acid, and a new reaction product is deposited on the surface of the workpiece. Still another reason is that different types of cleaning solutions used in the cleaning treatment chemically react with each other, and a new reaction product is generated on the

surface of the workpiece. The g neration of contamination due to th chemical reaction between the different types of cleaning solutions will be further described in d tail. In order to clean this type of workpiece, for example, cleaning treatment in which concentrated sulfuric acid immersion cleaning and alcohol immersion cleaning are combined is employed. In this cleaning treatment, after concentrated sulfuric acid immersion cleaning is performed in one vessel, pure water immersion cleaning is performed in three vessels b fore alcohol immersion cleaning in one vessel. Even if such pure water cleaning treatment is intervened, when foreign substances or the like exist on the surface of the workpiece or surface wettability of the workpiece is not uniform, sulfuric acid sticks and remains on the surface of the workpiece after pure water treatment and reacts with alcohol in the subsequent alcohol immersion cleaning. treatment to generate a kind of esterified reaction product. In such a case, it is difficult to remove contamination due to the reaction product even by cleaning again with a cleaning solution such as sulfuric acid or alcohol, which is particularly troublesome.

As described above, in the known wet cleaning method, it is difficult to completely remove contamination due to organic foreign substances stuck on the workpiece, and new contamination may occur on the surface of the workpiece

because f a reaction between the organic foreign substances and a claning solution or a reaction between the individual claning solutions.

The present invention overcomes the foregoing problems. It is an object of the present invention to provide a method for cleaning in which contamination due to organic foreign substances stuck on the surface of a workpiece can be completely removed and new contamination associated with cleaning treatment can be prevented.

[Means for Solving the Problems]

The present invention was made to achieve the object described above, and in a method for cleaning a hard surface having organic foreign substances with a cleaning solution, followed by drying, a step of irradiating the hard surface with ultraviolet light is provided before any given step of cleaning with the cleaning solution.

### [Operation]

By irradiating a workpiece with ultraviolet light before cleaning with a cleaning solution, organic foreign substances such as a photoresist that remain on the surface of the workpiece are subjected to a chemical reaction, and the organic foreign substances may be decomposed and disappear at that stage or may become to be easily dissolved or removed by a cleaning solution in the subsequent cleaning treatment with the cleaning solution. Therefore, the

organic f reign substances do not remain on the surface of the workpi ce after the cleaning treatment with the cleaning soluti n.

Additionally, by the ultraviolet radiation treatment, since the organic foreign substances do not exist on the surface of the workpiece any more during cleaning treatment, a new reaction product is not generated due to a chemical reaction between the organic foreign substances and the cleaning solution.

Moreover, since surface wettability of the workpiece is improved by the ultraviolet radiation treatment, the cleaning solution spreads over the surface of the workpiece uniformly, and cleaning treatment with the cleaning solution can be performed uniformly over the entire workpiece, and also draining is easily performed when the workpiece is withdrawn from the cleaning solution and the cleaning solution does not remain partially concentrated on a portion of the surface of the workpiece. Thereby, for example, in a cleaning method in which sulfuric acid immersion cleaning treatment and alcohol immersion cleaning treatment are combined, if a simple pure water immersion cleaning treatment step for eliminating sulfuric acid that remains slightly on the surface of the workpiece is provided between the sulfuric acid treatment and the alcohol treatment, new contamination due to a chemical reaction between sulfuric

acid and alcohol do s not occur.

### [Example]

With resp ct to a conventional m thod for cleaning a photomask in which a workpiece is subjected to sulfuric acid cleaning, pure water cleaning, and isopropyl alcohol (hereinafter abbreviated as IPA) cleaning in that order, followed by drying using IPA vapors, an example in which the workpiece is subjected to ultraviolet radiation treatment before sulfuric acid cleaning will be described below.

As a workpiece, a photomask obtained by the known steps of resist, etching, and photoresist stripping was used. That is, in order to obtain the photomask as a workpiece, AZ-1350 (manufactured by Hoechst) as a positive photoresist was applied on a photomask blank in which a chrome shading film was formed on a transparent glass substrate, exposure and development were performed through a mask having-a predetermined pattern, the shading film was etched using the resist pattern as a mask, and then the resist pattern was stripped.

Four sheets of such a photomask with dimensions of 5  $\times$  5  $\times$  0.09 inch were placed in an ultraviolet irradiation system (treatment-chamber volume: 3,240 cm<sup>3</sup>) and ultraviolet radiation treatment was performed.

Treating conditions are as follows.

Ultraviolet source: low-pressure mercury-vapor lamp,

in which the intensity of an emission line at 2,537 Å occupies 90% and the intensity of an emission line at 1,849 Å occupies several percents of the total intensity.

Total power applied to low-pressure mercury-vapor lamp: 770 W

Wet air: Introduced at a velocity of 30 l/minute from a gas inlet of the ultraviolet irradiation system.

Wet air improves the efficiency of O<sub>3</sub> generation during ultraviolet radiation.

Treating time: 5 minutes

After ultraviolet radiation treatment, the workpiece was subjected to cleaning treatment, followed by drying treatment. That is, cleaning treatment was performed by immersing the workpiece in one-vessel concentrated sulfuric acid having a concentration of 98% for 5 minutes, next by immersing in one-vessel pure water for 30 seconds, and further by immersing in one-vessel IPA for 3 minutes. With respect to the immersion of the workpiece in the IPA vessel, ultrasonic cleaning was performed by propagating ultrasonic waves into the IPA solution. (An ultrasonic oscillator for generating frequencies of 45 kHz and 46 kHz alternately was used. Applied power was 400 W.)

Drying treatment after the cleaning treatment was performed by exposing the workpiece withdrawn from the IPA

v ss l to IPA vapors.

With r spect to 16 workpiec s which w re cleaned and dried aft r ultraviolet radiation treatment as described above, the cleanliness level was inspected. Contamination was not observed in all 16 workpieces.

With respect to 15 workpieces which were cleaned and dried in a similar manner without performing ultraviolet radiation treatment, the cleanliness level was inspected. Contamination was observed in the entire surfaces of all 15 workpieces. Even when pure water immersion cleaning treatment was performed in three vessels and the immersion time was set for 100 seconds each, contamination was often observed in the entire surface of the workpiece when ultraviolet radiation was not performed.

As a result of this example, in the method in which ultraviolet radiation treatment is performed in accordance with the present invention, organic foreign substances stuck on the workpieces are effectively removed and a new reaction product associated with a chemical reaction during cleaning treatment is not generated, and thereby it is clear that cleanliness of the workpieces after cleaning treatment can be secured satisfactorily.

Although in the example described above, a photomask stuck with a residual positive (photodegradable) photoresist was used, in the method in accordance with the present

invention, a workpi c stuck with a residual negative (photo-setting) photoresist may be cl aned, and in the case of positiv and negative electron beam resists, the method also can be used similarly.

The method in accordance with the present invention is not limited to cleaning of photomasks. Photomask blanks, glass substrates, glass substrates provided with transparent conductive films, silicon wafers, and the like, and additionally, optical lenses such as camera lenses and spectacle lenses may be considered as workpieces, and the method is used to remove organic foreign substances (e.g., contaminants due to dust in air or contaminants due to finger contact) attached or stuck to the surfaces thereof.

Ultraviolet radiation conditions may be selected appropriately depending on materials of workpieces and processes undergone before cleaning treatment. That is, as a light source for ultraviolet radiation, a mercury arc lamp, a medium-pressure mercury lamp, a high-pressure mercury lamp, a xenon lamp, a heavy-water lamp, or the like may be used. As an induction gas, instead of wet air used in the example described above, dry air, ozone (O<sub>3</sub>), or the like may be used. Moreover, power and treating time may be varied voluntarily. Ultraviolet radiation may be performed in an atmosphere containing a gas such as oxygen, and in such a case, oxygen changes into ozone during ultraviolet radiation

and oxidative d struction or the like of contaminants stuck on the w rkpiece is accelerated. Ultraviolet radiati n may also be performed in an atmosphere containing an inert gas such as argon or nitrogen. Although ultraviolet light radiated may have a given wavelength in addition to that described in the example, in order to effectively reduce and remove foreign substances such as organic substances, it is desirable that ultraviolet light having a wavelength of 1,000 to 3,000 Å be radiated.

Although ultraviolet radiation treatment was performed before sulfuric acid cleaning in the example described above, the timing of ultraviolet radiation treatment is not limited to this in accordance with the method of the present invention. Ultraviolet radiation treatment may be performed after sulfuric acid cleaning and before pure water cleaning or after pure water cleaning and before IPA cleaning, or ultraviolet radiation treatment may be performed at least twice, for example, before sulfuric acid cleaning, and after sulfuric acid cleaning and before pure water cleaning.

With respect to cleaning treatment after ultraviolet radiation treatment, although sulfuric acid, pure water, and IPA were used in that order in the example described above, cleaning treatment used in the method of the present invention is not limited to this. For example, cleaning treatment using aqueous hydrogen peroxide only, IPA only, or

hydrog n peroxid and IPA may be adopted. In cleaning treatment using aqueous hydrogen p roxide only or IPA only, ultraviolet radiation treatment is performed before cleaning with aqueous hydrogen peroxide or IPA, and in cleaning treatment using aqueous hydrogen peroxide and IPA, ultraviolet radiation treatment is performed at a given stage before aqueous hydrogen peroxide cleaning, after aqueous hydrogen peroxide cleaning and before pure water cleaning, or after pure water cleaning and before IPA cleaning.

Of course, when a workpiece is subjected to immersion cleaning in a cleaning solution, ultrasonic waves may be propagated into the cleaning solution, or the workpiece may be oscillated.

As cleaning treatment, instead of immersing a workpiece in a cleaning solution as described above, a method-of spraying a cleaning solution while a workpiece is rotated by a spinner or the like, or a method of spraying a workpiece with a pressurized (high-pressure jet) cleaning solution may be adopted.

With respect to drying treatment of the workpiece, although vapor drying by IPA vapors was adopted in the example described above, vapor drying using other vapors such as flon may be used, or spin drying may be used.

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The method of the present invention is also effective

in r cl aning a workpi ce in which contamination has occurred due to a chemical reaction betw n diff r nt types of cleaning solutions (for xample, sulfuric acid and alcohol) as a result of carrying out a general cleaning process without ultraviolet radiation treatment. By recleaning treatment with a cleaning solution after ultraviolet radiation treatment, contamination that is not removable under normal conditions can be removed.

## [Advantages]

As described above in detail, the method in accordance with the present invention makes it possible to effectively clean photomasks, photomask blanks, glass substrates, semiconductor substrates, and the like, and also articles having hard surfaces such as optical lenses and spectacle lenses, and the industrial significance of the invention is great.

Applicant for Patent Hoya Corporation

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CLEANING OF HARD SURFACE

PUBLISHED: 63 -271938 [JP 63271938 A] November 09, 1988 (19881109)

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APPL. NO.: 62-106069 [JP 87106069] FILED: April 28, 1987 (19870428)

INTL CLASS: [4] HO1L-021/304; B08B-007/00; G03F-001/00

JAPIO CLASS: 42.2 (ELECTRONICS -- Solid State Components); 28.1

(SANITATION -- Sanitary Equipment); 29.1 (PRECISION

INSTRUMENTS -- Photography & Cinematography)

JOURNAL: Section: E, Section No. 723, Vol. 13, No. 97, Pg. 104, March

07, 1989 (19890307)

### ABSTRACT

PURPOSE: To prevent the occurrence of new contamination by a method wherein ultraviolet light is irradiated on the hard surface, whereon organic foreign substances exist, of a matter be cleansed before the matter to be cleansed is cleansed with a cleaning fluid.

CONSTITUTION: In case the hard surface, whereon organic foreign substances exist, of a matter to be cleansed is dried after being cleansed with a cleaning fluid, ultraviolet light is irradiated on the hard surface before the cleaning. That is, by irradiating the ultraviolet light on the matter to be cleansed before the matter to be cleansed is cleansed with the cleaning fluid, the organic foreign substances of a photo resist and so on remaining on the surface of the matter to be cleansed are subjected to chemical change, are decomposed and disappeared on the spot and are brought in a state that they are easy to dissolve or peel with the cleaning fluid in a cleaning treatment to be executed with a cleaning fluid subsequent to that. Thereby, it is eliminated that organic foreign substances remain on the surface of the matter to be cleansed after the matter to be cleansed is subjected to cleaning treatment with a cleaning fluid and the occurrence of new contamination can be prevented.